

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

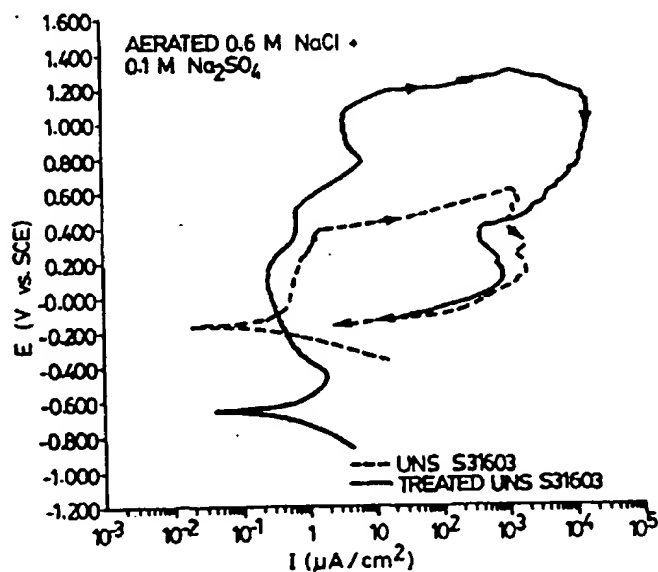
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C23C 22/48, 22/68		A1	(11) International Publication Number: WO 96/11290
			(43) International Publication Date: 18 April 1996 (18.04.96)
(21) International Application Number: PCT/CA95/00565		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).	
(22) International Filing Date: 10 October 1995 (10.10.95)		<p>Published</p> <p><i>With international search report.</i></p> <p><i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
(30) Priority Data: 9420295.9 7 October 1994 (07.10.94) GB			
(71) Applicant: McMASTER UNIVERSITY [CA/CA]; Office of Research, Hamilton, Ontario L8S 4L7 (CA).			
(72) Inventors: LU, Yucheng; 99 Bertram Drive, Dundas, Ontario L9H 4T8 (CA). IVES, Michael, Brian; 124 Lynn Court, Burlington, Ontario L7T 1B4 (CA).			
(74) Agents: SCHUMACHER, Lynn, C. et al.; Hill & Schumacher, Suite 1600, 372 Bay Street, Toronto, Ontario M5H 2W9 (CA).			

(54) Title: METHOD OF INCREASING CORROSION RESISTANCE OF METALS AND ALLOYS BY TREATMENT WITH RARE EARTH ELEMENTS

(57) Abstract

There is provided a method for treating the surface of metals such as ferritic steels, austenitic stainless steels, copper and aluminum alloys to increase their corrosion resistance. The metals are immersed into a heated aqueous composition containing a rare earth salt. Increased corrosion resistance is obtained using nitrates of yttrium, gadolinium, cerium, europium, terbium, samarium, neodymium, praseodymium, lanthanum, holmium, ytterbium, dysprosium, and erbium nitrates. The rare earth salt is present in the range from about 2% by weight to saturation of the solution. The composition includes a pH-modifying substance such as nitric acid to adjust the pH in the range 0.5 to about 6.5 to attack the surface to remove oxides facilitating deposition of the rare earth. For aluminum alloys the pH is maintained between 4.5 to 6.5, for nickel based alloys and austenitic stainless steels the pH is maintained between 0.5 to 3.5 and between pH 2.0 to 4.5 for ferritic stainless steels. The surface can also be conditioned by abrasion before or during immersion in the composition. Increased corrosion resistance is achieved by immersion for 15 to 20 minutes with the composition maintained between 60 to 95 °C. Gadolinium, neodymium and praseodymium nitrate when used alone produced the greatest degree of corrosion resistance compared to the other rare earth nitrates. Significant synergistic effects are observed when combinations of two or more rare earth nitrates are used in the compositions. Compositions based on cerium nitrate, gadolinium nitrate and lanthanum nitrate are very effective in reducing crevice corrosion.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

WO 96/11290

PCT/CA95/00565

METHOD OF INCREASING CORROSION RESISTANCE OF METALS AND ALLOYS BY TREATMENT WITH RARE EARTH ELEMENTS

FIELD OF THE INVENTION

5 The present invention relates to a process of increasing corrosion resistance of metals and alloys by surface treatment with one or more elements from the rare earth group of elements. More particularly, the present invention provides a method of increasing corrosion resistance of metals such as stainless steels, nickel based alloys, aluminum alloys and copper alloys in aqueous solutions by treatment in a solution of rare earth salts.

BACKGROUND OF THE INVENTION

10 Highly alloyed stainless steels and nickel based alloys are now utilized in environments which produce significant localized corrosion in many other metals and alloys. The excellent pitting corrosion resistance of these highly alloyed stainless steels and nickel based alloys is due to the high alloy composition, which is believed to inhibit the anodic processes. Of the beneficial alloying elements in
15 stainless steels, chromium is the most important because it forms a bipolar passive film, see A.R. Brooks, C.R. Clayton, K. Doss and Y.C. Lu, **J. Electrochem. Soc.**, Vol. 133, 2459, (1986). To date, the alloy development approach has been to increase the amount of alloyed chromium, molybdenum and nitrogen in order to improve pitting corrosion resistance. However, crevice corrosion remains a problem
20 in these alloys. For example, it can be manifest as under-deposit corrosion, as has been found in recent ocean tests even in steels with high molybdenum and chromium contents, see M.B. Ives, in Proceedings "Applications of Stainless Steels '92", **Jernkontoret**, Stockholm, 436 (1992).

25 The major difference between crevice and pitting corrosion involves the initiation stages. Crevice corrosion in aerated solutions involves an oxygen concentration cell. Furthermore, in the later stages of localized corrosion

WO 96/11290

PCT/CA95/00365

development, cathodic reduction of the depolarizers on the large areas surrounding the attacked site is necessary to support the high rate of anodic dissolution. It has been disclosed by Y.C. Lu, J.L. Luo and M.B. Ives, **ISI International**, Vol. 31, 210 (1991), that the enhanced cathodic reduction of oxidant adjacent to a localized attack site produces an increase of localized corrosion. Thus a powerful means of preventing crevice corrosion would be to constrain or significantly inhibit the cathodic reactions such as oxygen reduction, hydrogen evolution and the like.

It has been previously reported that cerium ion-implantation in UNS S31603 stainless steels effectively inhibits the reduction of oxygen and protons, reducing the rate by more than two orders of magnitude, see Y.C. Lu and M.B. Ives, **Corrosion Sci.**, Vol. 34, 11, 1773 (1993). Also, the anodic (passive) current density is reduced by more than one order of magnitude for UNS S31603 stainless steel after cerium implantation. Consequently, cerium ion implantation improves the crevice corrosion resistance of UNS S31603 stainless steel as determined by both anodic polarization in aerated 0.1 M Na₂SO₄ + 0.6 M NaCl solution and by the ASTM G48 B crevice test in 10% ferric chloride hexahydrate solution. However, ion-implantation is not readily amenable to economically treating large surface areas materials. Further, ion-implantation may induce radiation damage at the surface of the metal or alloy which may have detrimental structural effects so that ion-implantation has practical limitations.

Aluminum alloys are of commercial and industrial significance comparable or greater than that of stainless steels. Corrosion and corrosion induced failure is a major problem associated with aluminum alloys. Aluminum alloys are widely used in very corrosive environments, for example in automotive applications such as brazed aluminum heat exchangers, coolers, evaporators, radiators and the like. Known methods of corrosion protection of aluminum and aluminum alloys involve the use of chromate ions to form conversion coatings on the alloys. Environmental concerns associated with chromate ions are a drawback to widespread use of this technique. Other strategies for increasing corrosion resistance of aluminum based alloys based on physical deposition methods such

WO 96/11290

PCT/CA95/00565

as sputtering are inherently limited since the area being coated is by line-of-sight from the source.

Cerium containing solution treatment has been effective in improving the localized corrosion resistance of aluminum alloys. For example, it has previously been reported that chemical passivation of aluminum alloys immersed in cerium chloride solutions for 7 days or longer produces a conversion coating on the aluminum alloy exhibiting increased corrosion resistance, see F. Mansfield, S. Lin, S. Kim and H. Shih, *J. Electrochem. Soc.*, Vol. 137, 78 (1990). In order to speed up the production of the conversion coating, the aluminum alloys have dipped into hot cerium salt solutions followed by direct current (DC) anodic polarization in a molybdate solution to produce an anodized passive layer containing Ce and Mo as disclosed in F. Mansfield, V. Wang and H. Shih, *J. Electrochem. Soc.*, Vol. 138, L74 (1991). Alternating current (AC) passivation of aluminum alloys in the same types of cerium salt solutions has also been used to form conversion coatings exhibiting corrosion resistance as disclosed in H. Shih, V. Wang and F. Mansfield, *Corrosion* 91, Paper # 136, NACE, Houston (1991). The use of rare earth metal chlorides as inhibitors for aluminum alloys in NaCl has been disclosed in D.R. Amott, B.R.W. Hinton and N.E. Ryan, *Corrosion*, Vol. 45, 12 (1989).

For the foregoing reasons, there has been a need for a simple, inexpensive, and rapid surface treatment for increasing the corrosion resistance of industrially important metals and alloys such as copper and copper alloys, chromium, molybdenum, ferritic and austenitic stainless steels, nickel based alloys, aluminum alloys and the like which is environmentally safe.

SUMMARY OF THE INVENTION

The present invention provides compositions and a method for increasing the corrosion resistance of metals and alloys by exposing the surface of the metals to the compositions. The compositions may be used to treat chromium, molybdenum, nickel, copper, a range of austenitic and ferritic stainless

WO 96/11290

PCT/CA95/00565

steels, nickel based alloys, aluminum and aluminum alloys, copper and copper alloys, chromium, molybdenum, nickel and the like to improve the localized corrosion resistance of the alloys. The corrosion behaviour of treated and untreated samples has been compared using a combination of electrochemical measurement techniques in an aerated 0.6M NaCl + 0.1M Na₂SO₄ solution, corrosion tests and field tests in natural seawater. Surface analysis has been used to determine the chemical composition of the films formed on the treated surfaces in order to elucidate the mechanism of the enhanced corrosion-resistance. The surface analysis and electrochemical studies indicate the surface of the alloys is modified upon exposure to the compositions and exhibits improved resistance to localized corrosion and especially crevice corrosion resistance in chloride containing media. The effect is very appreciable for the crevice corrosion resistance of austenitic stainless steels and nickel based alloys in sea water or chlorinated seawater.

The present invention provides a method of treating metals and alloys to increase corrosion resistance. The method comprises exposing a surface of a metal or alloy to an aqueous composition at an effective temperature. The aqueous composition comprises a salt of at least one rare earth element. The composition comprises a pH-modifying agent present in an amount effective to adjust the pH to from about 0.5 to about 6.5 to condition the surface to enhance deposition of the rare earth element thereon.

The at least one rare earth salt is selected from the group of salts consisting of yttrium, gadolinium, cerium, europium, terbium, samarium, neodymium, praseodymium, lanthanum, holmium, ytterbium, dysprosium and erbium and substantially excluding rare earth salts containing halides. The at least one rare earth salt being present in an amount of from about 2% by weight to saturation. The surface may be abraded prior to or during exposure to the aqueous composition.

In another aspect the invention is directed to a method of treating metals or alloys to increase their corrosion resistance. The method comprises

WO 96/11290

PCT/CA95/00565

conditioning a surface of the metal or alloy to substantially remove metal oxide present on the surface and exposing the surface to an effective amount of at least one of the rare earths under conditions sufficiently energetic to incorporate some of the rare earths into the surface.

5 The step of conditioning the surface and exposing the surface includes immersing the metal or alloy in a composition comprising a rare earth salt, but not rare earth halides, in the range from about 2% by weight to saturation, and a pH modifying substance in an amount sufficient to adjust the pH to an effective value in the range from about 0.5 to about 6.5 to facilitate deposition of the rare
10 earth thereon. The step of conditioning may include abrasion of the surface before or during immersing the metal or alloy in the aqueous composition.

 The present invention provides a method for treating the surface of ferritic stainless steels, austenitic stainless steels, chromium, molybdenum, copper, copper alloys, aluminum and aluminum alloys to increase their corrosion
15 resistance. The method comprises exposing the surface of the metal to a heated composition comprising an aqueous solution of a salt of at least one rare earth element selected from the group consisting of salts of yttrium, gadolinium, cerium, europium, terbium, samarium, neodymium, praseodymium, lanthanum, holmium, ytterbium, dysprosium and erbium. The composition comprises a pH-modifying
20 agent in an amount sufficient to adjust the pH from about 0.5 to about 6.5.

 The rare earth salt is present in the amount of from about 2% by weight to saturation. Where the metal is a ferritic stainless steel the pH is adjusted to a value from about 2 to about 4.5, for treating austenitic stainless steels and nickel based alloys, the pH is adjusted to between about 0.5 to about 3.5, for
25 treating aluminum alloys the pH is adjusted to between about 4.5 to about 6.5, and the temperature of the aqueous solution is maintained in the range from about 60°C to about 95°C.

 In another aspect of the invention a composition for treating metals and alloys to increase their corrosion resistance is provided. The composition
30 comprises an aqueous solution of a salt of at least one rare earth element, the

WO 96/11290

PCT/CA95/00565

5 rare earth element being selected from the group consisting of salts of gadolinium, yttrium, cerium, europium, terbium, samarium, neodymium, praseodymium, lanthanum, holmium, ytterbium, dysprosium and erbium. The rare earth salt is present in an amount of from about 2% by weight to saturation and the composition includes a pH-modifying agent in an amount effective to adjust the pH from about 0.5 to about 6.5. The composition is preferably substantially exclusive of rare earth salts containing halides.

BRIEF DESCRIPTION OF THE DRAWINGS

10 The method of increasing corrosion resistance of metals and alloys by treatment with compositions containing rare earth elements in accordance with the present invention will now be described, by example only, reference being had to the accompanying drawings, in which:

15 Figure 1 is a plot of disc current vs. potential for both treated (0.05M $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ at 90-95°C for 1 hour) and untreated UNS N08904 stainless steel discs in aerated 0.1 M Na_2SO_4 + 0.6 M NaCl solution at pH 8.26;

Figure 2 displays disc current measured from Figure 1 at -950 mV vs. the square root of the angular velocity of the rotating discs;

20 Figure 3 displays the potentiodynamic polarization curves of treated and untreated UNS S31603 steel in aerated solution at pH 8.26;

Figure 4 shows SIMS profiles from UNS S31603 stainless steel samples treated at $95 \pm 2^\circ\text{C}$ for 1 hour in distilled water;

Figure 5 shows SIMS profiles from UNS S31603 stainless steel samples treated at $95 \pm 2^\circ\text{C}$ for 1 hour in 0.05 M cerium nitrate;

25 Figure 6 shows galvanostatic polarization curves of UNS S40900 samples before and after treatment in 0.1 M gadolinium nitrate, neodymium nitrate and praseodymium nitrate at 85°C for 20 minutes;

30 Figure 7 shows galvanostatic polarization curves of UNS S40900 samples before and after treatment in 0.1 M cerium, europium, samarium, terbium and ytterbium nitrate at 85°C for 20 minutes;

WO 96/11290

PCT/CA95/00565

Figure 8 shows galvanostatic polarization curves of UNS S40900 samples before and after treatment in 0.1 M erbium, yttrium, lanthanum, dysprosium and holmium nitrate at 85°C for 20 minutes;

5 Figure 9 shows potentiodynamic polarization plots of UNS S40900 stainless steel samples before and after treating in 0.4M cerium nitrate, gadolinium nitrate, and a mixture of 0.1 M gadolinium nitrate and 0.3 M cerium nitrate at 85°C for 20 minutes;

10 Figure 10 is a flow chart summarizing the weight loss results of UNS S31603 alloy samples after 24 hours of ASTM G48 B testing at 22°C after treatment in each of the indicated rare earth salt containing solutions;

Figure 11 illustrates the weight loss after 24 hours ASTM G48 B testing at 22°C for UNS S31603 stainless steel samples treated in solutions of 0.3 M cerium nitrate plus an additional 0.1 M of the different indicated rare earth nitrates including cerium nitrate;

15 Figure 12 illustrates the weight loss after 24 hours ASTM G48 B test at 22°C for UNS S31603 stainless steel samples treated in solutions listed in Table II at 22°C for 20 minutes;

20 Figure 13 shows the galvanostatic polarization plots of the UNS S40900 stainless steel samples before and after being treated in formulation A described hereinafter, formulation B described hereinafter, formulation A with 30% nitric acid, formulation B with 30% nitric acid, and 30% nitric acid alone;

Figure 14 shows potentiodynamic polarization plots of UNS S40900 stainless steel samples before and after treating in formulation A alone and in formulation A with 10 ppm and 100 ppm of Fe^{+3} contamination;

25 Figure 15 shows the galvanostatic polarization plots of UNS S40900 stainless steel samples before and after treating in formulation A alone and in formulation A with 10 ppm and 100 ppm of Fe^{+3} contamination;

30 Figure 16 displays galvanostatic polarization curves for UNS S40900 samples treated in formulation A with 100 ppm of Fe^{+3} contamination before and after recovery of the solution, compared with a control sample untreated;

WO 96/11290

PCT/CA95/00565

Figure 17 shows potentiodynamic polarization plots of a brazing aluminum alloy sample treated using a rare earth salt solution according to the present invention and the same alloy treated using a commercial chromate treatment; and

5 Figure 18 shows potentiodynamic polarization plots of copper alloy samples treated with rare earth salt solutions discussed hereinafter.

DETAILED DESCRIPTION OF THE INVENTION

10 The following description of the method of increasing corrosion resistance of metals and alloys will first describe the treatment of various stainless steels using compositions containing only one rare earth salt, followed by a description of the treatment of various stainless steel alloys, nickel, nickel based alloys, aluminum alloys, chromium, iron and copper alloys using compositions comprising more than one rare earth element.

15 As used herein, the term rare earth element refers to the lanthanide series of elements in the periodic table with proton numbers ranging from cerium (58) to lutetium (71) inclusive. Lanthanum, yttrium and scandium, while not technically lanthanides because they do not have f-orbital electrons, are chemically very similar to the lanthanides and accordingly are also considered rare earth elements herein. While the term rare earths specifically refers to the oxides of the rare earth elements, it is used more generally to refer to this particular group of elements both in chemical practise and hereinafter.

20 While the term rare earths specifically refers to the oxides of the rare earth elements, it is used more generally to refer to this particular group of elements both in chemical practise and hereinafter.

A) Corrosion Inhibition By Treatment With Individual Rare Earth Elements

i) Cerium Containing Solutions

25 The samples of Table I were electrochemically characterized and in addition were subjected to surface analysis and the results of these studies are shown in Figures 1 to 5.

30

WO 96/11290

PCT/CA95/00565

Table I
Composition of Stainless Steels Used In This Study (wt %)

Elements Alloys	Cr	Ni	Mo	Cu	Mn	C	P	S	Si
UNS S40900	11.0	0.5	-	-	1.0	0.08	0.045	0.045	1.0
UNS S31603	17.0	12.0	2.5	-	2.0	0.03	0.045	0.03	1.0
UNS N08904	20.0	24.8	4.72	1.60	1.61	0.012	0.020	0.002	0.37

Figure 1 shows the disc current vs. potential for UNS N08904 stainless steel discs, before and after exposure to a cerium nitrate containing composition, cathodically polarized in an aerated 0.1 M Na_2SO_4 + 0.6 M NaCl solution (pH = 8.26) at different disc rotation speeds. The data indicates that for the untreated UNS N08904 disc the cathodic current is rotation-speed dependent. The cathodic reaction rates, i.e. cathodic currents on the cerium-treated electrodes are shifted to more negative potentials and are greatly restrained. The current for oxygen reduction does not apparently depend on rotation speed.

Figure 2 shows the disc current, measured from UNS N08904 discs at -950mV, as a function of the square root of disc angular velocity. The straight line fit of the data indicates the reduction of oxygen on the untreated stainless steel is mass transport limited. However, the current measured on the cerium-treated UNS N08904 steel was greatly reduced and did not depend significantly on rotation speed. The data show clearly that the cathodic electrode reaction is inhibited by the cerium nitrate treatment. The electrode process is controlled predominantly by charge transfer processes at the electrode surface.

The cerium pretreatment was also found to influence the anodic characteristics of these stainless steels. In Figure 3, the anodic polarization of untreated and treated UNS S31603 steel are compared. In addition to the cathodic inhibition which shifted the open circuit potential by about 480 mV, the passive

WO 96/11290

PCT/CA95/00565

range was extended greatly by cerium treatment. The breakdown potential has been raised about 800 mV. The passive current density was also reduced significantly. This result indicates that the cerium treatment also stabilizes passivity and inhibits breakdown.

5 Auger electron spectroscopy (AES) and secondary ion mass spectroscopy (SIMS) profiles showed that the Cr/Fe ratio of the surface film formed on cerium-treated UNS S31603 was about twice that of the same steel treated in distilled water at the same temperature. This is illustrated by comparing the SIMS
10 profiles in Figures 4 and 5, which also indicate that cerium is present in the oxide film on the treated steel. The increased concentration of chromium in the surface region suggests an important effect of cerium treatment on the improved stability of the passive film. The distribution of cerium over the surface was however not uniform (data not shown).

X-ray photoelectron spectroscopy (XPS) has previously been used
15 to help identify the chemical state of the cerium present on treated surfaces. The position of the $3d^{5/2}$ peak was determined to be ≈ 888 eV, which compares with values for a $\text{Ce}(\text{NO}_3)_3$ standard of ≈ 889 eV, and a CeO_2 standard of ≈ 882 eV (data not shown). Clearly the cerium was present in a trivalent form. A very small amount of nitrogen was also detected by XPS analysis on cerium treated steel,
20 and its peak position (≈ 401 eV) may suggest the presence of NO^- rather than nitrate (408 eV) or nitride (397 eV). The oxygen spectrum showed both O^{2-} and OH^- signals of about equal intensity. The above results suggest that cerium may form Ce^{3+} complexes or oxy-hydroxide in the surface of the treated steels.

Further evidence for the ability of a non-uniform distribution of cerium
25 to significantly inhibit the cathodic reaction processes has been provided by direct evidence that the cathodic sites are themselves not uniformly distributed. A modified crevice test was performed on UNS S40900 stainless steel immersed in a copper-containing solution of 0.5% $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ + 0.5% $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ at 22° C. The corrosive attack on the treated steel was observed to be much lighter than on
30 the untreated one. But in addition copper nodules were deposited on the exposed

WO 96/11290

PCT/CA95/00565

areas surrounding the crevice sites. These are caused by cathodic reduction from cupric ion to metallic copper, indicating that the cathodic reactions do not take place on the entire surface uniformly. Since the cerium is likewise non-uniformly deposited, it is attractive to account for its inhibition effectiveness through the formation of Ce^{3+} complexes or oxy-hydroxide which block the dispersed active cathodic reaction sites.

Similar studies were conducted to determine the efficacy of cerium treatment on pure iron, nickel, molybdenum and chromium. Cerium treatment of iron did not result in an observable improvement in corrosion resistance of the iron, based upon comparison of galvanostatic and potentiodynamic scans on treated and untreated samples (data not shown).

Treatment of pure nickel did result in an increase in corrosion resistance determined from a comparison of galvanostatic and potentiodynamic scans on treated and untreated samples (data not shown).

Treatment of molybdenum and chromium samples in cerium nitrate containing compositions resulted in a significant increase in corrosion resistance for both metals (data not shown) with molybdenum exhibiting a greater degree of corrosion resistance than molybdenum.

The role of the cerium treatment with metals or alloys with chromium present appears to be to produce a surface region enriched with chromium with the cerium oxide/oxyhydroxide either blocking the active sites for cathodic reduction or inhibiting electron transfer through the film.

II) Other Rare Earth Element Solutions

Referring to Figures 6 through 8, galvanostatic polarization curves are displayed for UNS S40900 samples before (control) and after treatment in solutions containing the indicated rare earth species. Specifically, the UNS S40900 samples were treated in 0.1M concentrations of eleven different rare earth salts. The UNS S40900 samples were dipped in the different lanthanide nitrate solutions at 85°C for about 20 minutes. The samples were galvanostatically polarized in aerated 0.6M NaCl + 0.1M Na_2SO_4 solution at a current density of $-10\mu A/cm^2$. The

WO 96/11290

PCT/CA95/00565

steady state potential reached for each sample, referred to herein as E_{Final} , was used as an indicator of the degree of cathodic inhibition produced by each treatment.

Referring to Figure 6, the E_{Final} for samples treated in 0.1 M gadolinium nitrate, neodymium nitrate and praseodymium nitrate are each about -1000 mV(SCE). Referring to Figure 7, samples treated in solutions containing cerium, europium, samarium, terbium and ytterbium nitrates exhibited E_{Final} values of about -600 mV (SCE). Samples treated in solutions containing erbium, yttrium, lanthanum, dysprosium and holmium nitrates exhibited values for E_{Final} of about -550 mV(SCE), see Figure 8. The galvanostatic polarization plot for untreated UNS S40900, labelled "control", exhibited a value for E_{Final} of about -430mV(SCE).

These results clearly show that the cathodic reaction kinetics of these alloys are significantly inhibited upon exposure of the surfaces all lanthanide nitrate solutions tested at elevated temperatures. Treatment in gadolinium nitrate produces the greatest degree of cathodic inhibition followed closely by treatment in neodymium and praseodymium nitrates. The results of Figures 6 to 8 were obtained by treatment in solutions containing 0.1M concentrations of the various lanthanide nitrates, however, corrosion inhibition was observed in solutions containing lanthanide concentrations ranging from 2% up to saturation. The remaining rare earth elements including scandium, lutetium, thulium and promethium were not tested but the inventors contemplate that treatment with their corresponding nitrates would also provide similar results in view of the fact that inhibition was unexpectedly obtained with all the rare earths tested and the chemical behaviour of the lanthanides are very similar.

In addition to the nitrates of the rare earth elements, compositions using rare earth chlorides were tested. The chlorides exhibited no efficacy for increasing the corrosion resistance of the steels. The ineffectual nature of the rare earth chlorides may be understood in view of the fact that the presence of chlorides in particular, and halide ions in general, are known to cause the breakdown of passive films formed on most metals including stainless steels.

WO 96/11290

PCT/CA95/00565

B) SYNERGISTIC EFFECT OF COMBINATIONS OF RARE EARTH ELEMENTS ON CATHODIC INHIBITION

According to the electrochemical data of Figures 6 to 8, samples treated with individual solutions of gadolinium nitrate, neodymium nitrate and praseodymium nitrate exhibit the highest degree of cathodic inhibition for the single rare earth containing compositions. The inventors have further discovered that combinations of rare earths unexpectedly produce a synergistic effect for cathodic inhibition. Figure 9 displays four potentiodynamic polarization plots for an untreated UNS S40900 sample, a sample treated in 0.4M gadolinium nitrate, a sample treated in 0.4M cerium nitrate and a sample treated in a composition containing 0.1M gadolinium nitrate and 0.3M cerium nitrate solution, all treated samples being exposed to the compositions for 20 minutes at 85°C. The formulation containing the combination of gadolinium nitrate and cerium nitrate showed significant improvement in cathodic inhibition of UNS S40900 samples as compared to samples treated in the compositions containing the individual rare earth nitrates. It is clearly seen from the results of Figure 9 that at the same total molarity, using a combination of cerium and gadolinium nitrate produces a cathodic inhibition on the cathodic reaction kinetics superior to the inhibition achieved with the individual nitrates.

Figure 10 is a flow chart showing the effect of different binary and ternary combinations of lanthanides on weight loss resulting from crevice corrosion tests for UNS S31603 stainless steel samples. To test the synergistic effect of the combinations of lanthanides in improving the crevice corrosion resistance, UNS S31603 stainless steel samples were treated in solutions containing 0.3M cerium nitrate in combination with 0.1M concentrations of other different lanthanum nitrates. For comparison, samples treated in 0.4M cerium nitrate and control samples were tested in parallel. The pH of all solutions was adjusted to 1.32 ± 0.01 except for the solution using cerium nitrate alone. After the treatment, the samples were tested by the ASTM G48 B standard method at 22°C for 24 hours. The weight loss was recorded and is presented graphically in Figure 11.

WO 96/11290

PCT/CA95/00565

More detailed corrosion inhibition studies of binary and many combinations of gadolinium nitrate, praseodymium nitrate, neodymium nitrate, cerium nitrate and lanthanum nitrate on UNS S31603 samples were conducted using the different combinations/concentrations given in Table II below.

Table II

Solutions for UNS S31603 Treatment Summarized In Figure 12

Label	Solution
Ce3La1	0.3M cerium nitrate + 0.1M lanthanum nitrate
Ce3Gd1	0.3M cerium nitrate + 0.1M gadolinium nitrate
Ce2La1Gd1	0.2M cerium nitrate + 0.1M lanthanum nitrate + 0.1M gadolinium nitrate
Gd3Nd1	0.3M gadolinium nitrate + 0.1M neodymium nitrate
Gd3Pr1	0.3M gadolinium nitrate + praseodymium 0.1M nitrate
Gd3Pr1Nd1	0.3M gadolinium nitrate + praseodymium 0.1M nitrate + 0.1M neodymium nitrate
Control	Sample without treatment

Note: pH of all solutions was adjusted to 1.32 ± 0.01 .

The resulting weight loss values are summarized in Figure 12. The results show that exposure of the samples for 20 minutes to compositions at 85°C containing cerium, lanthanum and gadolinium are very effective in increasing the crevice corrosion resistance of the alloys. This was determined by the 10% ferric chloride hexahydrate crevice test (ASTM G48 B Test) at 22°C for 24 hours.

The results show that combinations of two or more lanthanide nitrates produce a greater degree of corrosion inhibition than using a composition having only one rare earth element present. Combinations of lanthanum, cerium, gadolinium, neodymium and praseodymium nitrates all exhibit an efficacy for corrosion inhibition superior to the individual nitrates alone.

As described below two example formulations, one a binary

WO 96/11290

PCT/CA95/00565

combination of lanthanide salts, and the other being a ternary combination of lanthanide salts, have been tested and shown, by laboratory accelerated corrosion tests and seawater field tests, to be very effective in improving the crevice corrosion resistance of various alloys.

5 Formulation A: 130.3 g/l of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 45.0 g/l of $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with the pH adjusted to within the range 0.5 - 6.5 depending on the alloys or metals being treated.

10 Formulation B: 130.3g/l of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 45.0 g/l of $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 43.5 g/l of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with the pH adjusted within the range 0.5 to 6.5 depending on the metal or alloy being treated.

15 Significant corrosion inhibition was obtained with Inconel 625 pipe samples treated using compositions based on cerium nitrate alone and formulation B. No crevice corrosion was detected on samples treated with formulation B after 30 days exposure to seawater while the untreated samples showed crevice corrosion after only six days of seawater exposure.

20 The major parameters of the compositions produced in accordance with the present invention are the use of one or more rare earth salt(s), pH range of the composition, temperature of the composition to which the surface of the metal is being exposed, and residence time of the metal therein. The residence time may be limited to from about 15 minutes to about an hour at elevated temperatures (about 60°C to 95°C). Lower temperatures of the compositions necessitate longer exposure times. For example, at ambient temperature, exposure times of the order of several days are required to achieve the corrosion resistance effect obtained for 15 minutes exposure at elevated temperatures. Surface conditioning methods other than by exposure to acid solutions, such as mechanical or other chemical processes may also be variables to consider.

25 In order to achieve the satisfactory treatment effect, the pH value of the aqueous composition should be adjusted in an appropriate range depending on the metal or alloy being treated. Increase in the acidity of the solution to a certain level enhances the surface enrichment of beneficial alloy elements for

-15-

Ce	140	$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	$= 140 + 3(14) + 9(16) + 12 + 6(16)$
Gd	157		$= 434$
La	14	$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	$= 157 + 3(14) + 9(16) + 12 + 6(16)$
	16		$= 451$
			433
La	14		

WO 96/11290

PCT/CA95/00565

passivity. However, if the solution pH drops beyond certain values, the effect on cathodic inhibition will be weakened. The galvanostatic polarization plots of Figure 13 illustrates the effect of 30% nitric acid addition can diminish the cathodic inhibition. It also causes attack to the substrate and results in rapid degradation of the treatment solution when treating ferritic stainless steels. The inventors have found that the pH should be adjusted in the range of about 0.5 to about 3.5 for austenitic stainless steels and nickel based alloys and in the range from about 2 to about 4.5 for ferritic stainless steel. The pH of the solution may be adjusted by adding nitric acid to the solution.

The optimum treatment parameters can be adjusted according to the metals to be treated. Formulations A and B given above are nonlimiting examples. While treatment in these formulations produce significant corrosion inhibition on stainless steels, it will be appreciated that many other compositions of varying rare earth salt components and concentrations produced in accordance with the present invention will provide improvement in corrosion resistance of alloys.

Detergents or surfactants may be added to the compositions for cleaning the metal surfaces. For example, a commercial surfactant such as ARMAK 1997 (Akzo Chemicals Inc) may be added to the treatment solution at 0.5-1.0% for samples having surfaces contaminated with for example processing lubricating oils and finger prints which may obstruct effective chemical treatment. The choice of surfactant will be determined in part by the solubility of the surfactant in the composition for the particular pH value. The metal to be cleaned and conditioned may initially be immersed in a preconditioning bath including an acid in addition to a surfactant.

Mechanical abrasion of the surface of the metal prior to exposure to the lanthanides has been observed to be beneficial increase the efficacy of the corrosion inhibition effect. This effect is possibly due to the breaking up of an existing oxide layer on the metal surface which may impede the surface reactions leading to the corrosion inhibition effect. Using abrasion in combination with the aggressive aqueous compositions are expected to reduce the residence time of

WO 96/11290

PCT/CA95/00565

the metal or alloy workpiece in the compositions. Thus mechanical abrasion of metals and alloys being treated by the method disclosed herein is advantageous where native oxide layers are expected to be present and the lanthanide is being integrated into the surface in a method different than using the aqueous compositions of low pH.

The efficacy of the compositions disclosed herein for economically treating large quantities of metals or alloys depends on long term stability of the compositions. The present compositions were found to be very stable with no observable precipitation or degradation over a period of three years.

During constant use of the compositions for treating large quantities of metal, certain materials will accumulate in the treatment bath over time. Ferric ions will build up in solution which changes the acidity of the bath. Addition of sodium hydroxide may be used to control the change in acidity. Therefore, studies were conducted to determine the effect of ferric ion concentration and sodium concentration on the efficacy of the compositions.

Due to selected dissolution of iron during exposure of iron based alloys to the compositions, ferric ions will accumulate in the solution resulting in a more aggressive solution. The effect of ferric ion on the performance of the compositions was studied by adding $\text{Fe}(\text{NO}_3)_3$ to formulation A containing 0.3 M cerium nitrate and 0.1M gadolinium nitrate. The addition of 10 ppm and 100 ppm of Fe^{3+} into formulation A resulted in a reduction in the pH of the formulations from 2.53 to 2.47 and 2.13 respectively. After treating a UNS S40900 alloy steel sample at 85°C for 20 minutes in formulation A with 10% ferric ions, the sample was observed to be slightly etched due to the hydrolysis of the cations and the pH value of the solution dropped to 1.82. When 1000 ppm ferric ions were added to formulation A, the solution became cloudy and Fe_2O_3 precipitated out. The solution was very aggressive and vigorously attacked the treated stainless steel samples.

The adverse effect of the presence of ferric ion on the corrosion inhibition performance is readily apparent from the polarization plots in Figure 14 and Figure 15. As the concentration of the ferric ion increases in formulation A, the

WO 96/11290

PCT/CA95/00565

efficacy of the formulations toward cathodic inhibition decrease. The tolerance level of the ferric ion is below 100 ppm. It is important to remove the accumulated ferric ions from the solution. By adjusting the pH of the formulation to 2.5-2.8 with dilute sodium hydroxide, the ferric ion can be precipitated from the solution as ferric hydroxide and ferric oxide. The effectiveness of the formulation for corrosion inhibition may be recovered by allowing the precipitate to settle followed by filtering. The galvanostatic polarization plot of Figure 16 was obtained on a UNS S40900 sample treated in formulation A originally contaminated by 100 ppm Fe^{3+} . The formulation was subsequently recovered as discussed above and from Figure 16 it is clear the recovered formulations exhibit effective cathodic inhibition.

Sodium nitrate will also accumulate in the treatment compositions as a result of bath maintenance. The effect of sodium content in the treatment formulations was studied by adding sodium nitrate to formulation A at three levels, 0.1M, 0.5M, and 1M. Potentiodynamic polarization plots on UNS S40900 samples in formulation A with the above levels of sodium nitrate showed the presence of sodium had no discernable adverse effects on the corrosion inhibition behaviour (data not shown).

Figure 17 is a potentiostatic polarization plot for a brazing aluminum alloy before and after treatment in a solution comprising formulation A diluted by a factor of 7 using water. The alloy was a two-sided clad brazing sheet comprising a core material consistent with AA4045 aluminum alloy and a lower melting Al-Si clad layer on both sides of the core. The composition of the double clad aluminum material was:

Element	Core	Clad
Silicon	0.40 max.	9.0-11.0
Iron	0.50 max.	0.50 max.
Copper	0.20-0.40	0.10 max.
Manganese	1.0-1.25	0.10 max.
Magnesium	0.35-0.55	0.10-0.30
Titanium	0.15 max.	-----
Zinc	0.15 max.	0.10 max.
Other	0.05 ea.	0.05 ea.
Other Tot.	0.15 max.	0.15 max.
Aluminum	remainder	remainder

W 96/11290

PCT/CA95/00565

The brazing samples were subjected to a typical brazing cycle (heating to 1100°F for 1-3 minutes in dry nitrogen atmosphere) prior to testing so that the samples were tested in the as brazed condition. The samples were rinsed in acetone and then immersed in diluted formulation A as previously described. The formulation was "aged" by immersing an aluminum sample therein for 8 hours at 85°C after the samples were immersed in the formulation for 1 hour at 85°C. For comparison, aluminum alloy samples were subjected to a chromate treatment in a 4% by volume chromate solution at 35 to 40°C for 2.7 minutes. The samples were tested for corrosion resistance in a 5% solution of auto coolant, "ZEREX", BASF 340-2 which also contained 150 ppm salts as follows: 0.2077 g/liter NaHCO₃, 0.2231 g/liter Na₂SO₄ and 0.2487 g/liter NaCl heated to 75°C stirred with a glass impeller. The corrosion studies comprised free corrosion potential monitoring and cyclic polarization scans. From the cyclic polarization scans the pitting potential and corrosion resistance, R_p , were determined as follows:

Treatment	Control	Cr ⁶⁺	Rare Earth
Corr. Rate, R_p	3.945	0.207	0.713
Pitting E_p , V(SCE)	-0.200	0.180	0.130

From the cyclic scans of Figure 17 and the calculated corrosion resistance it can be seen that the rare earth treatment significantly increases the corrosion resistance of the brazed aluminum alloys.

A series of other compositions were tested which were found to increase the corrosion resistance of the aluminum alloy. The preferred pH range for solutions used to treat aluminum alloys is between 4.5 and 6.5. At pH values below 4.5 the dissolution of aluminum is excessive. Compositions for treating aluminum preferably include aluminum salts in order to reduce the corrosive attack on the alloy by the composition. The salts can be added directly to the compositions, for example aluminum nitrate was added directly and was found to be effective in the range of about 5 to 10 grams of the nitrate per liter of the

WO 96/11290

PCT/CA95/00565

composition. Alternatively, the salt can be generated in the composition by aging, that is, by placing a piece of aluminum into the freshly prepared composition.

Figure 18 is a potentiostatic polarization plot of a C12200 phosphorous deoxidized copper sample before and after treatment in a composition containing 130.3 g/l of cerium nitrate, and 45.0 g/l gadolinium nitrate and 10 g/l $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The pH was adjusted to 1 with HNO_3 and the solution heated to 350C. The copper samples were first cleaned in 10% H_2SO_4 and then rinsed in acetone prior to treatment in the rare earth salt solutions. The samples were tested for corrosion resistance in a 5% solution of auto coolant, "ZEREX", BASF 340-2 which also contained 150 ppm salts as follows: 0.2077 g/liter NaHCO_3 , 0.2231 g/liter Na_2SO_4 and 0.2487 g/liter NaCl heated to 750C stirred with a glass impeller. The corrosion studies comprised free corrosion potential monitoring and cyclic polarization scans. Several samples were tested in the same composition but for different periods of time with the cyclic potentiodynamic scans for a control sample not exposed to the formulation and samples exposed for 1, 2 and 3 minutes.

From the cyclic polarization scans of Figure 18 the pitting potential and corrosion resistance, R_p , were determined as follows:

Time min.	0 Control	1	2	3
Corr. Rate R_p mpy	21.99E-3	16.69E-3	11.75E-3	7.72E-3
Pitt. E_p V(SCE)	0.490	0.625	0.660	0.620

Although the corrosion rate of the copper samples was low in the test solution, the rare earth salt treatment successfully reduced the corrosion rate to a third of the untreated value. As with aluminum alloys, compositions for treatment of copper and its alloys preferably contains aluminum salts to reduce corrosive attack on the copper. Copper salts may also be used alternative to aluminum salts. The pH of the compositions is preferably adjusted in the range of 1 to 6.5. The

WO 96/11290

PCT/CA95/00565

data of Figure 18 shows that the method of the present invention may be advantageously used to increase the corrosion resistance of copper and its alloys.

SEAWATER CREVICE CORROSION STUDIES

The effect of the treatment on the crevice corrosion resistance of different kinds of stainless steels was evaluated by field seawater tests. The chemical composition of the stainless steels tested is given in Table III below. Samples were cut into 25 x 50 mm for sea water crevice tests. Prepared samples were wet ground with 600 grid emery paper and then ultrasonically cleaned with acetone, dried with clean air before further treatment or testing.

Table III

Composition of Relevant Stainless Steels Used in This Study (wt %)

Elements Alloys	Cr	Ni	Mo	Cu	Mn	C	P	S	Si	N
UNS S30403	19.0	9.7	-	-	2.0	0.03	0.045	0.03	1.0	-
UNS S31603	17.2	10.1	2.10	-	1.45	0.021	0.032	0.011	0.59	.06
UNS N08904	20.1	24.7	4.38	1.42	1.65	0.013	0.029	0.004	0.35	0.07
UNS N08925	20.60	24.70	6.10	0.88	0.86	0.006	0.018	0.002	0.37	0.198
UNS S31254	19.8	17.9	6.06	0.65	0.45	0.019	0.022	0.001	0.33	0.20
UNS N08367	20.42	23.76	6.23	-	0.34	0.029	0.021	0.001	0.37	0.23
AVESTA 654SMO	24.6	21.9	7.3	0.4	-	0.015	-	-	-	0.487
VDM 2803Mo	29.00	3.95	2.41	-	0.29	0.006	0.017	0.002	0.24	0.020

*: VDM Cronifer 2803Mo also comprises 0.43% Nb, 0.03% Co and 0.002% B.

WO 96/11290

PCT/CA95/00565

The composition used for the treatment of the samples comprised 0.05M cerium nitrate and the samples were treated at 90 to 95°C for 1 hour at a pH between 2.5 to 2.9. Samples for seawater field tests were mounted in treated and untreated pairs for visual comparison. A "TEFLON" crevice washer provided twelve crevice sites on each side of the sample. The sea water tests were performed both in brackish water in a channel and in chlorinated brackish water in an outlet trough of a testing rig. Parallel tests for treated and untreated tubes were also conducted in a simulated heat exchanger rig.

Table IV below summarizes the effect of cerium treatment in improving the crevice corrosion resistance of stainless steels in brackish water and chlorinated seawater.

Table IV

Crevice Corrosion Sites Observed On Samples After Field Test In (2ppm) Chlorinated Brackish Water For 24 Days

Sample Condition	UNS S30403	UNS S31603 #1	UNS S31603 #2	UNS N08904 #1	UNS N08904 #2	UNS N08925 #1-#3	UNS S31254 #1 & #2	AVEST A 654SMO #1 & #2
Untreated	5	7	5	5	5	0	0	0
Cerium Treated	0	0	0	0	0	0	0	0

Table IV shows that the treatment of UNS S30403, S31603 and N08904 significantly reduced or eliminated crevice corrosion in brackish water chlorinated with 2 ppm free chlorine for 24 days. Most of the untreated control samples of the same material exhibited significant crevice corrosion. Samples of untreated 6 Mo super stainless steels exhibited significant crevice corrosion after immersion in 2ppm chlorinated brackish water for 60 days.

WO 96/11290

PCT/CA95/00565

Table V below illustrates that cerium treatment resulted in crevice corrosion resistance of stainless steels immersed in chlorinated seawater.

Table V

Crevice Corrosion Sites Observed On Samples After Field Test In Chlorinated Seawater For 60 Days In 2 ppm Chlorinated Brackish Water

Sample Condition	VDM 2803Mo	UNS S31603	UNS N08367	UNS N08925
Untreated	0	18	1	4
Cerium Treated	0	12	0	0

Table VI below summarizes the results of steel samples after 100 days of testing in brackish seawater. The effect of the treatment in improving the crevice corrosion resistance in the harsh seawater environment is quite significant.

Table VI

Crevice Corrosion Sites Observed On Samples After Field Test In Brackish Water For 100 Days

Sample Condition	UNS S304 03 #1	UNS S304 03 #2	UNS S316 03	UNS N089 04	UNS N0892 50	UNS S31254	AVEST A 654SM O
Untreated	20	19	3	2	1	0	0
Cerium Treated	0	4	0	0	0	0	0

The studies of corrosion inhibition on various metals and alloys disclosed herein have shown that the cathodic reduction reactions occurring on

WO 96/11290

PCT/CA95/00565

stainless steel surfaces in a seawater environment are controlled by the mass transport of oxygen and/or protons in the solution. Chemical treatment with cerium nitrate effectively inhibits the cathodic kinetics of the oxygen reduction by impeding the charge transfer at the electrode, reducing the rate by more than one order of magnitude. The same treatment alters the reduction of protons on stainless steels from a mass transport controlled reaction to a reaction under mixed control resulting in the cathodic reduction of protons being restrained and the reaction occurring at higher overvoltage than for untreated steel.

Aqueous compositions using gadolinium nitrate alone give the most improvement in corrosion resistance compared to compositions using the other rare earth nitrates alone. There is a significant synergism among lanthanides in inhibiting the electrode kinetics, especially cathodic kinetics. The pH of the compositions for each the ferritic and austenitic stainless steels is preferably adjusted to assist in the surface enrichment of beneficial alloy elements such as chromium and molybdenum. At pH values too low the metal or alloy will undergo dissolution at rates too high to have a beneficial effect on cathodic inhibition.

Seawater field tests provided solid evidence for the effect of the lanthanide chemical treatment in improving the crevice corrosion resistance of variety of austenitic stainless steels including 6 Mo super stainless steels and inconel alloy. Lanthanide chemical treatment increases the localized corrosion resistance of ferritic stainless steel UNS S40900 in salt contaminated auto coolant.

Surface analysis confirmed that both the enrichment in the chromium content of the surface film and the cathodic inhibition resulting from the blocking effect of the active sites by lanthanide complexes or oxyhydroxide are responsible for the increased resistance of austenitic stainless steels to crevice corrosion.

In the surface treatment method using the aqueous compositions disclosed herein, the surface of the metal or alloy is activated by the pH of the composition. In addition to chemical activation of the surface by using compositions with low pH, mechanical abrasion may be used as an alternative or in combination with chemical activation. Using mechanical abrasion initially to

WO 96/11290

PCT/CA95/00565

condition the surface followed by immersion in the composition would facilitate use of higher pH values since a primary effect of the pH is to condition the surface. For deposition of the rare earths using processes other than aqueous compositions, surface activation may be achieved using mechanical abrasion, sputter etching, particle bombardment and the like.

The metal or alloy being treated could be subject to a pretreatment by immersion in an acid bath absent the rare earth salts in order to condition the surface after which the workpiece would be immersed into the particular composition containing the rare earth salt(s).

The preferred method disclosed herein of increasing the corrosion resistance of metals comprises exposing the surface of the metal to an aqueous composition containing one or a combination of lanthanides. The use of a liquid solution allows full access to the surface area of any shape of workpiece. However, it will be understood that other methods of treating the surface of a metal may be used, including sputtering, plasma spraying and the like, wherein rare earths are deposited on the alloy surface. Those skilled in the art would be able to determine the operative processing conditions for each deposition procedure.

The method disclosed herein is useful for treating products fabricated from commercial alloys which are used in environments prone to aqueous corrosion. The treatment may be carried out after production of the metal or alloy itself or after the product has been produced from the alloy. After a product has been produced from the alloy, it can be treated in a composition specifically optimized for the particular material and corrosive environment in which the product will be used.

While the compositions and method of treating metals and alloys for increasing corrosion resistance has been described and illustrated with respect to certain combinations of lanthanides, it will be readily apparent to those skilled in the art that numerous variations of these combinations may be made without departing from the scope of the invention described herein.

WO 96/11290

PCT/CA95/00565

THEREFORE WHAT IS CLAIMED IS:

1. A method of treating metals and alloys to increase corrosion resistance, comprising:
 - 5 exposing a surface of a metal or alloy to an aqueous composition at an effective temperature, the aqueous composition comprising a salt of at least one rare earth element, and a pH-modifying agent present in an amount effective to adjust the pH to from about 0.5 to about 6.5 to condition the surface to enhance deposition of the rare earth thereon.
- 10 2. The method according to claim 1 wherein said at least one rare earth salt is selected from the group consisting of salts of yttrium, gadolinium, cerium, europium, terbium, samarium, neodymium, praseodymium, lanthanum, holmium, ytterbium, dysprosium and erbium, but substantially exclusive of rare earth salts containing halides, the at least one rare earth salt being present in an amount of
15 from about 2% by weight to saturation,
3. The method according to claim 2 further comprising including abrading the metal or alloy surface prior to exposure to the aqueous composition.
20
4. The method according to claim 2 wherein the metal or alloy is a ferritic stainless steel and the pH is adjusted to from about 2 to about 4.5, and the temperature of the aqueous composition is from about 60°C to about 95°C.
- 25 5. The method according to claim 2 wherein the metal or alloy is selected from the group consisting of austenitic stainless steels and nickel based alloys, and the pH is adjusted to from about 0.5 to about 3.5, and the temperature of the aqueous composition is from about 60°C to about 95°C.
- 30 6. The method according to claim 2 wherein the metal or alloy is a aluminum

WO 96/11290

PCT/CA95/00565

or an aluminum alloy, and wherein the pH is adjusted to a value from about 4.5 to about 6.5, and the temperature of the aqueous composition is from about 60°C to about 95°C.

5 7. The method according to claim 2 wherein the metal or alloy is copper or a copper alloy, and wherein the pH is adjusted to a value from about 0.5 to about 6.5, and the temperature of the aqueous composition is from about 60°C to about 95°C.

10 8. The method according to claim 2 wherein said at least one rare earth salt is gadolinium nitrate.

9. The method according to claim 2 wherein said at least one rare earth salt is a combination of gadolinium nitrate and cerium nitrate.

15

10. The method according to claim 2 wherein the composition comprises a surfactant.

20

11. A method of treating metals or alloys to increase corrosion resistance, comprising:

 conditioning a surface of the metal or alloy to remove metal oxide present on the surface; and

 exposing the surface to at least one of the rare earth elements under conditions effective to incorporate some of said rare earth elements into the surface.

25

12. The method according to claim 11 wherein the step of conditioning the surface comprises mechanically abrading the surface.

30

13. The method according to claim 11 wherein the steps of conditioning and

WO 96/11290

PCT/CA95/00565

5 exposing the surface comprises immersing the metal or alloy in an aqueous composition comprising said least one of the rare earth elements in an amount of from about 2% by weight to saturation, and a pH modifying agent in an amount effective to adjust the pH to from about 0.5 to about 6.5 to facilitate deposition of the rare earth element thereon.

10 14. The method according to claim 13 wherein said at least one rare earth salt is selected from the group consisting of salts of yttrium, gadolinium, cerium, europium, terbium, samarium, neodymium, praseodymium, lanthanum, holmium, ytterbium, dysprosium and erbium, and substantially exclusive of rare earth salts containing halides.

15 15. A method for treating the surface of ferritic stainless steels, austenitic stainless steels, chromium, molybdenum, copper, copper alloys, aluminum and aluminum alloys to increase their corrosion resistance, comprising:

20 exposing the surface of the metal to a heated composition comprising an aqueous solution of a salt of at least one rare earth element selected from the group consisting of salts of yttrium, gadolinium, cerium, europium, terbium, samarium, neodymium, praseodymium, lanthanum, holmium, ytterbium, dysprosium and erbium, the rare earth salt being present in the amount of from about 2% by weight to saturation, and a pH-modifying agent in an amount sufficient to adjust the pH from about 0.5 to about 6.5.

25 16. The method according to claim 15 comprising abrading the surface before the step of exposing the surface.

17. The method according to claim 15 wherein said at least one rare earth salt is gadolinium nitrate.

30 18. The method according to claim 15 wherein said at least one rare earth salt

WO 96/11290

PCT/CA95/00565

is a combination of gadolinium nitrat and cerium nitrat .

19. The method according to claim 15 wherein said at least one rare earth salt is a combination of gadolinium nitrate, neodymium nitrate and praseodymium nitrate.

20. The method according to claim 15 wherein the composition comprises a surfactant.

21. A composition for treating metals and alloys to increase corrosion resistance, comprising:

an aqueous solution of a salt of at least one rare earth element, the rare earth element being selected from the group consisting of salts of gadolinium, yttrium, cerium, europium, terbium, samarium, neodymium, praseodymium, lanthanum, holmium, ytterbium, dysprosium and erbium, the rare earth salt being present in an amount of from about 2% by weight to saturation; and

a pH-modifying agent in an amount effective to adjust the pH from about 0.5 to about 6.5.

22. The composition according to claim 21 wherein said salt of at least one rare earth element is substantially exclusive of rare earth salts containing halides.

23. The composition according to claim 22 wherein said at least one rare earth salt is gadolinium nitrate.

24. The composition according to claim 22 wherein said at least one rare earth salt is a combination of gadolinium nitrate and cerium nitrate.

25. The composition according to claim 22 wherein said at least one rare earth salt is a combination of gadolinium nitrate, neodymium nitrate and praseodymium

WO 96/11290**PCT/CA95/00565**

nitrate.

26. The composition according to claim 22 wherein the composition comprises a surfactant.

WO 96/11290

PCT/CA95/00565

1/11

904L AND Ce/904L ROTATING DISK
AERATED 0.6M NaCl + 0.1M Na₂SO₄ pH 8.26

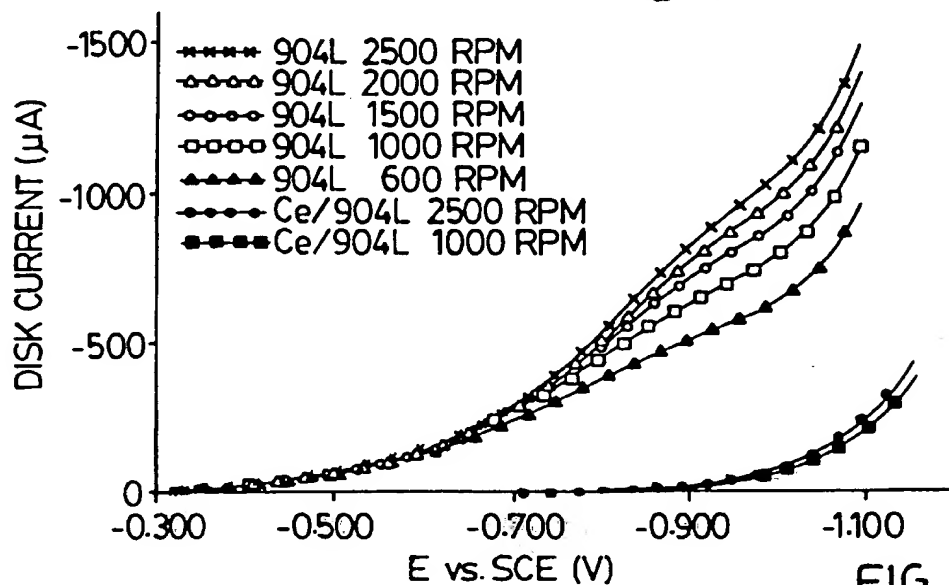


FIG. 1

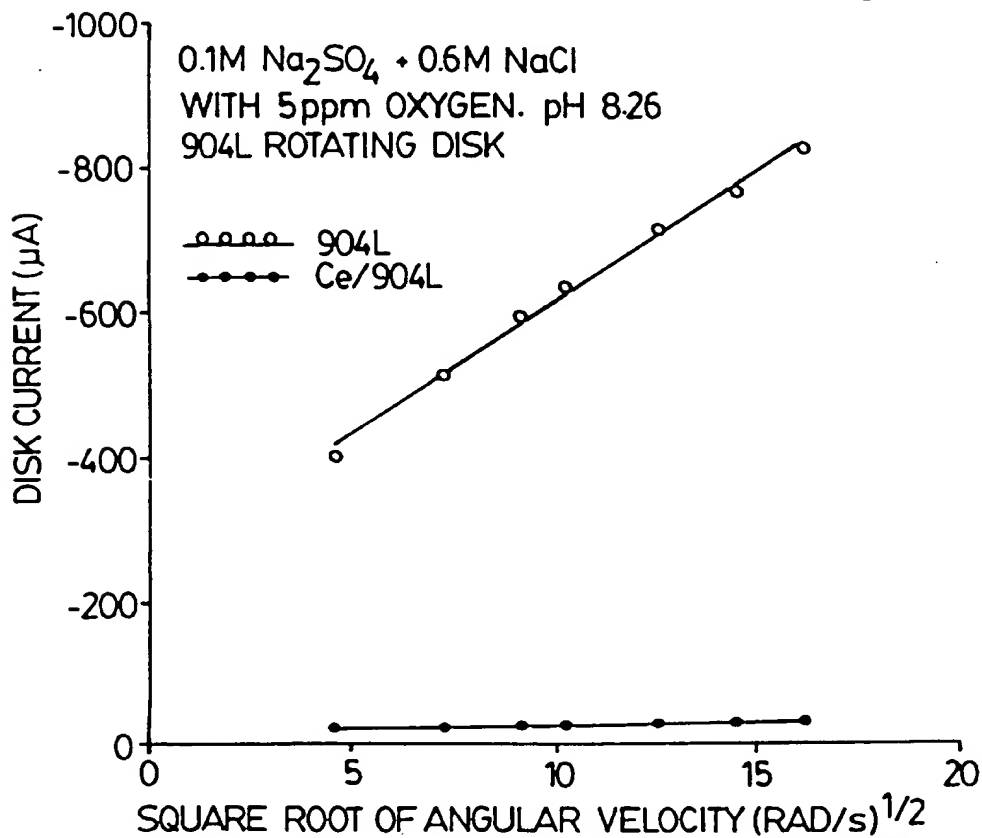


FIG. 2

WO 96/11290

PCT/CA95/00565

2/11

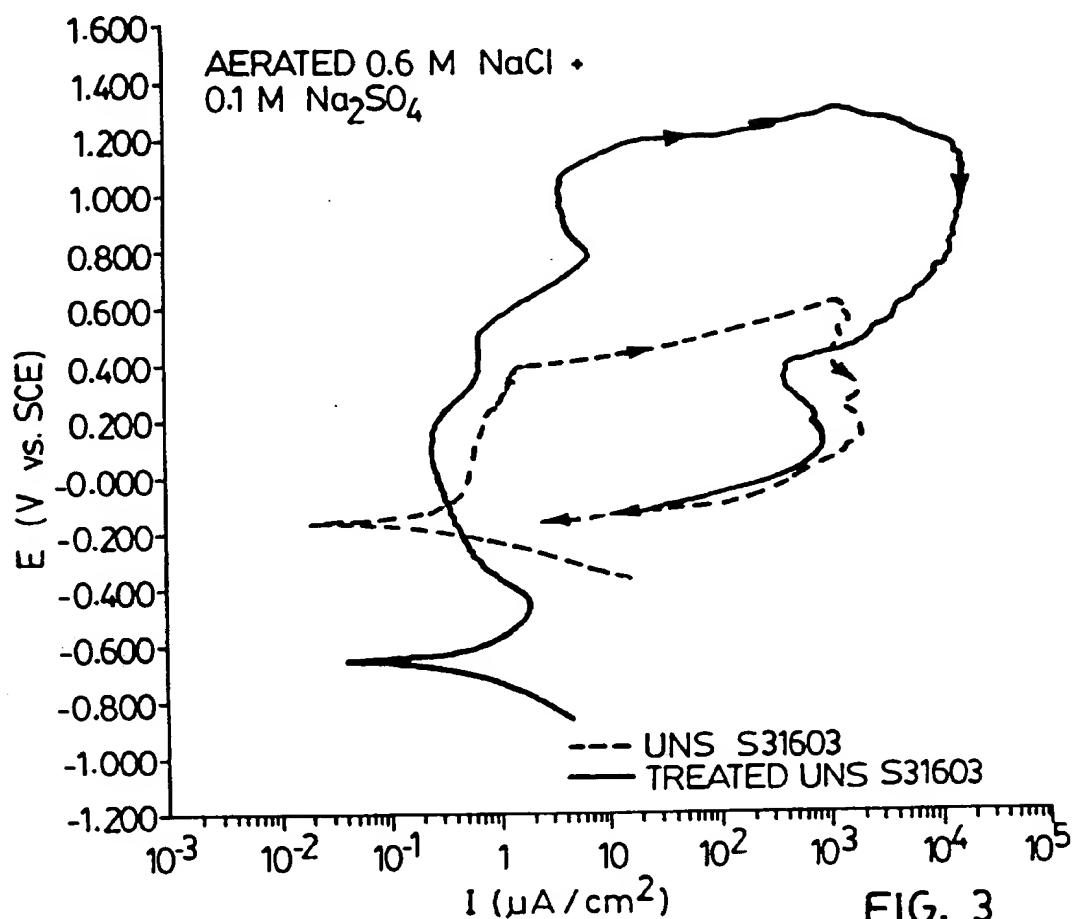


FIG. 3

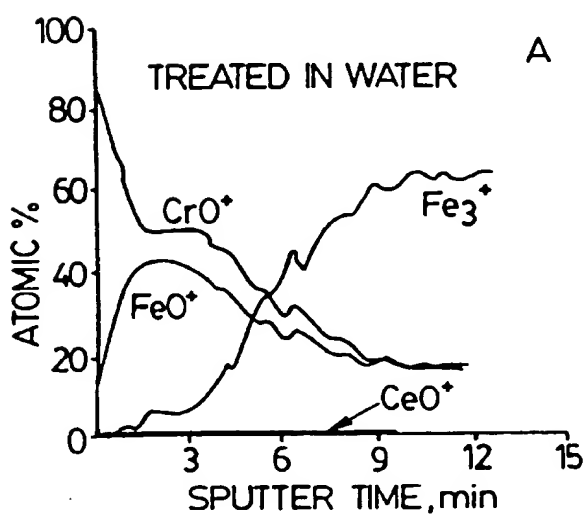


FIG. 4

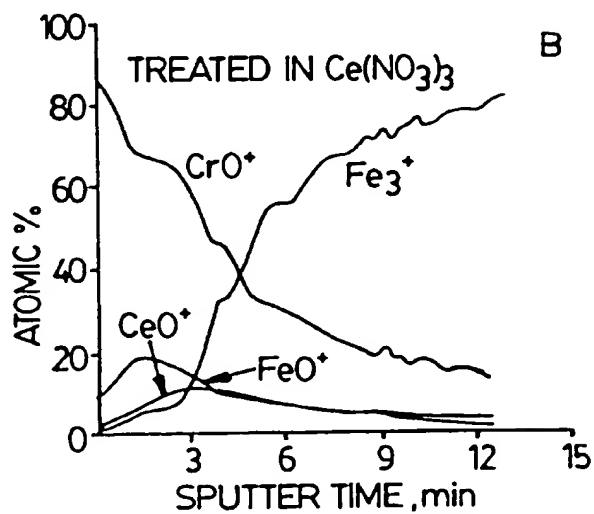
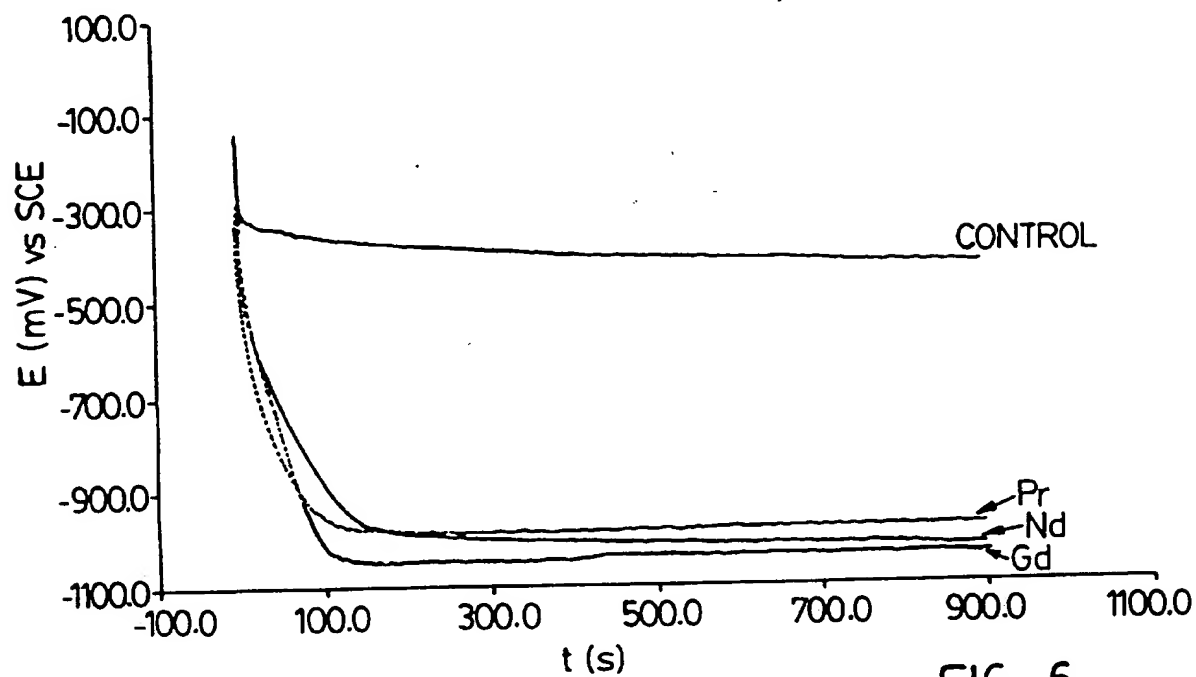
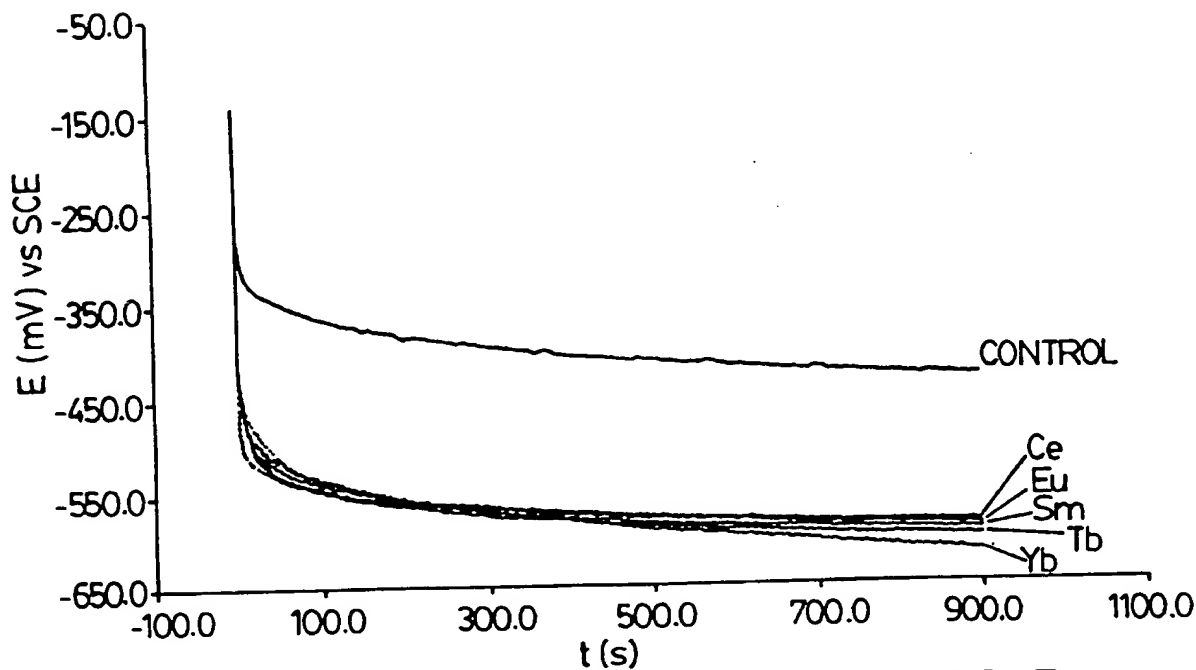


FIG. 5

WO 96/11290

PCT/CA95/00565

3/11

FIG. 6FIG. 7

WO 96/11290

PCT/CA95/00565

4/11

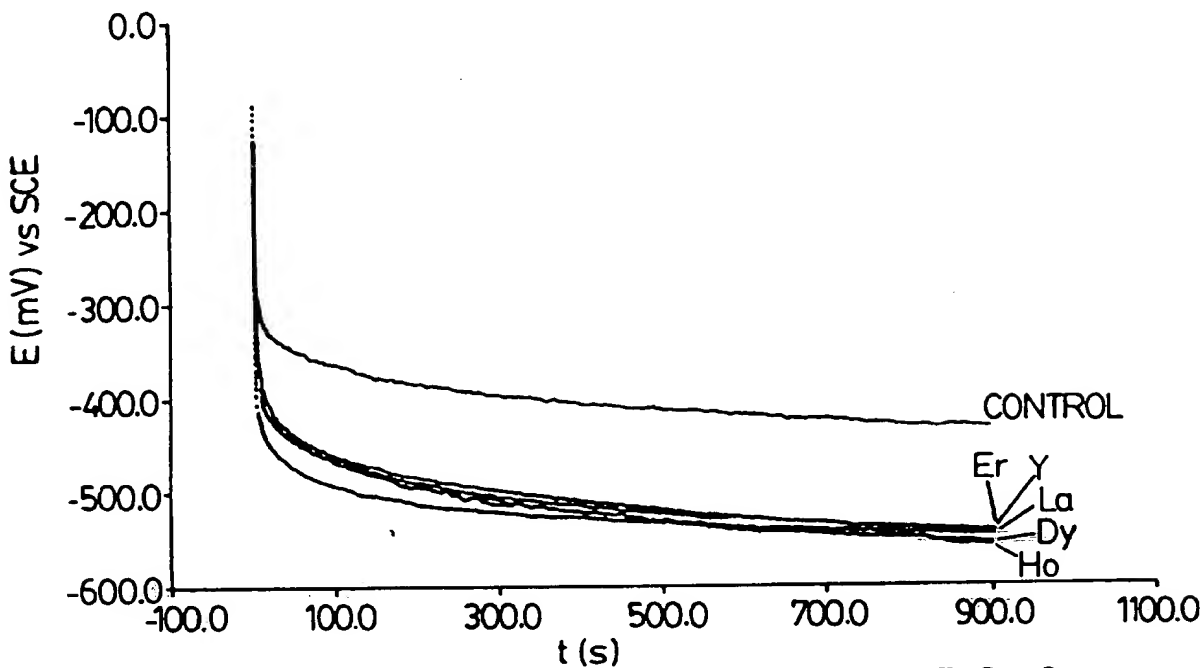


FIG. 8

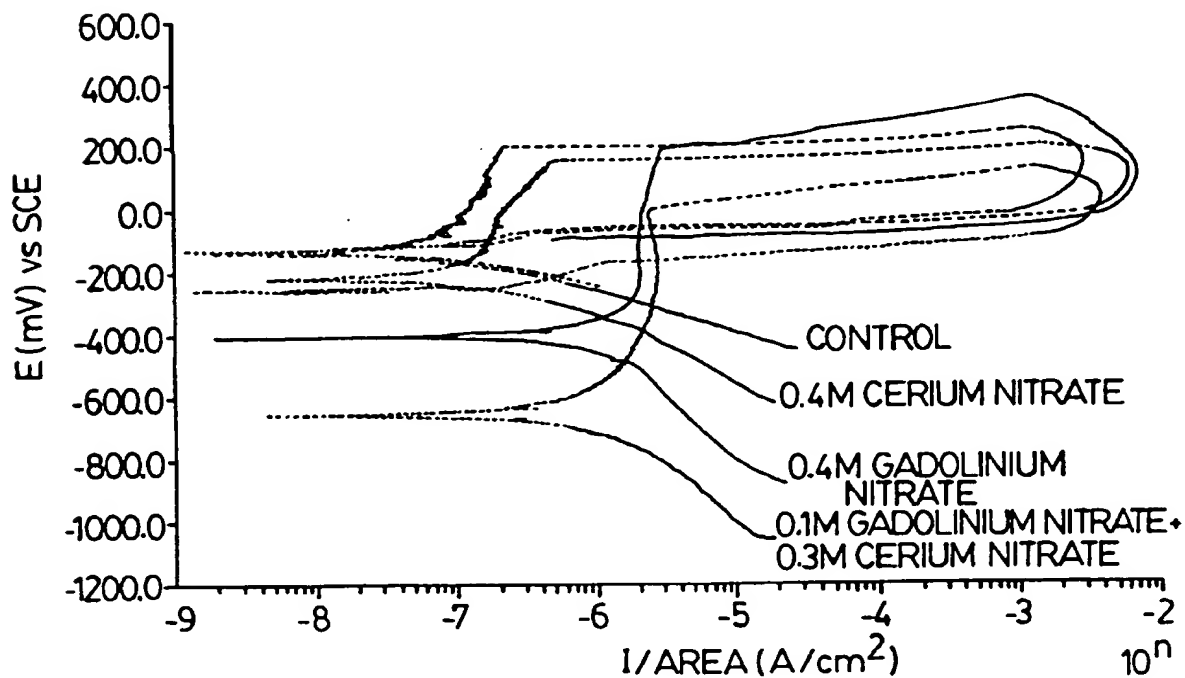


FIG. 9

WO 96/11290

PCT/CA95/00565

5/11

CONTROL UNS S31603
 $\Delta W = 66.7$ mg

0.3 M $\text{Ce}(\text{NO}_3)_3$
pH = 2.89
 $\Delta W = 28.4$ mg

0.3 M $\text{Ce}(\text{NO}_3)_3$
pH = 1.33
 $\Delta W = 20.3$ mg

0.3 M $\text{Gd}(\text{NO}_3)_3$
pH = 1.33
 $\Delta W = 14.7$ mg

0.3 M $\text{La}(\text{NO}_3)_3$
pH = 1.33
 $\Delta W = 21.1$

0.3 M $\text{Ce}(\text{NO}_3)_3$
0.1 M $\text{Gd}(\text{NO}_3)_3$
pH = 1.33
 $\Delta W = 13.4$ mg

0.3 M $\text{La}(\text{NO}_3)_3$
0.01 M $\text{Gd}(\text{NO}_3)_3$
pH = 1.33
 $\Delta W = 15.7$ mg

0.3 M $\text{Ce}(\text{NO}_3)_3$
0.1 M $\text{Gd}(\text{NO}_3)_3$
0.01 M $\text{La}(\text{NO}_3)_3$
pH = 1.33
 $\Delta W = 9.0$ mg

0.3 M $\text{Ce}(\text{NO}_3)_3$
0.1 M $\text{Gd}(\text{NO}_3)_3$
0.1 M $\text{La}(\text{NO}_3)_3$
pH = 1.33
 $\Delta W = 6.4$ mg

FIG. 10

WO 96/11290

PCT/CA95/00565

6/11

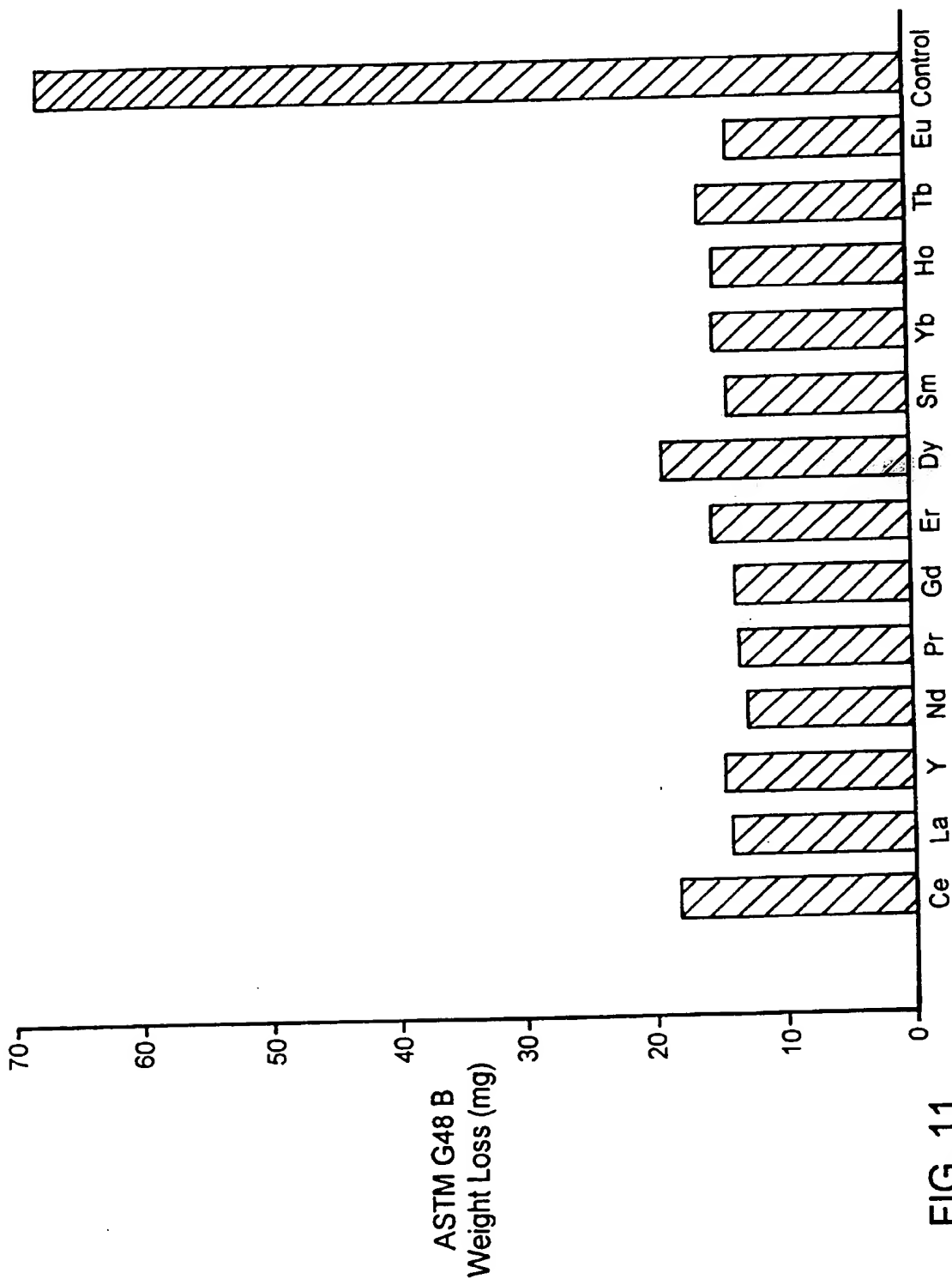


FIG. 11

WO 96/11290

PCT/CA95/00565

7/11

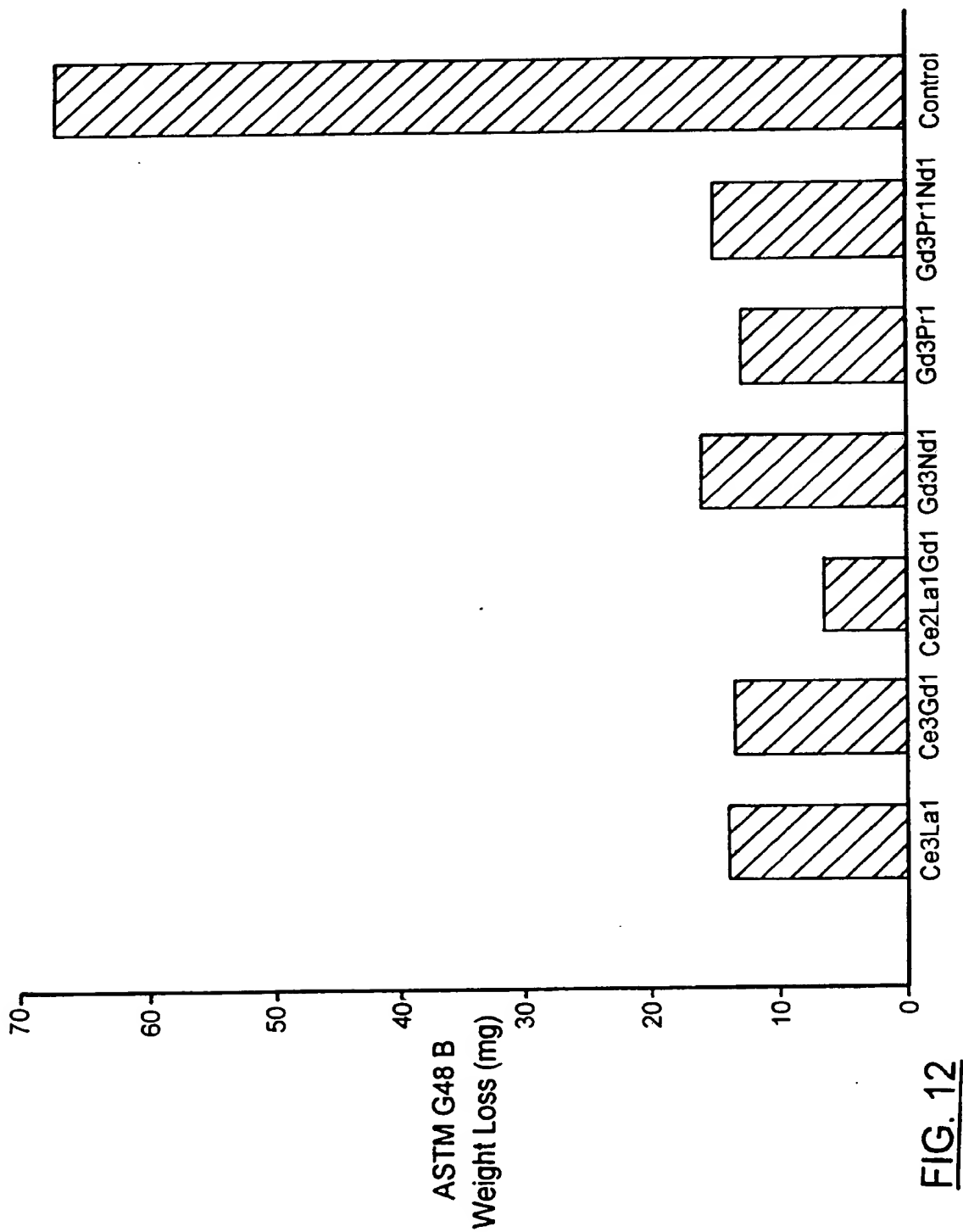
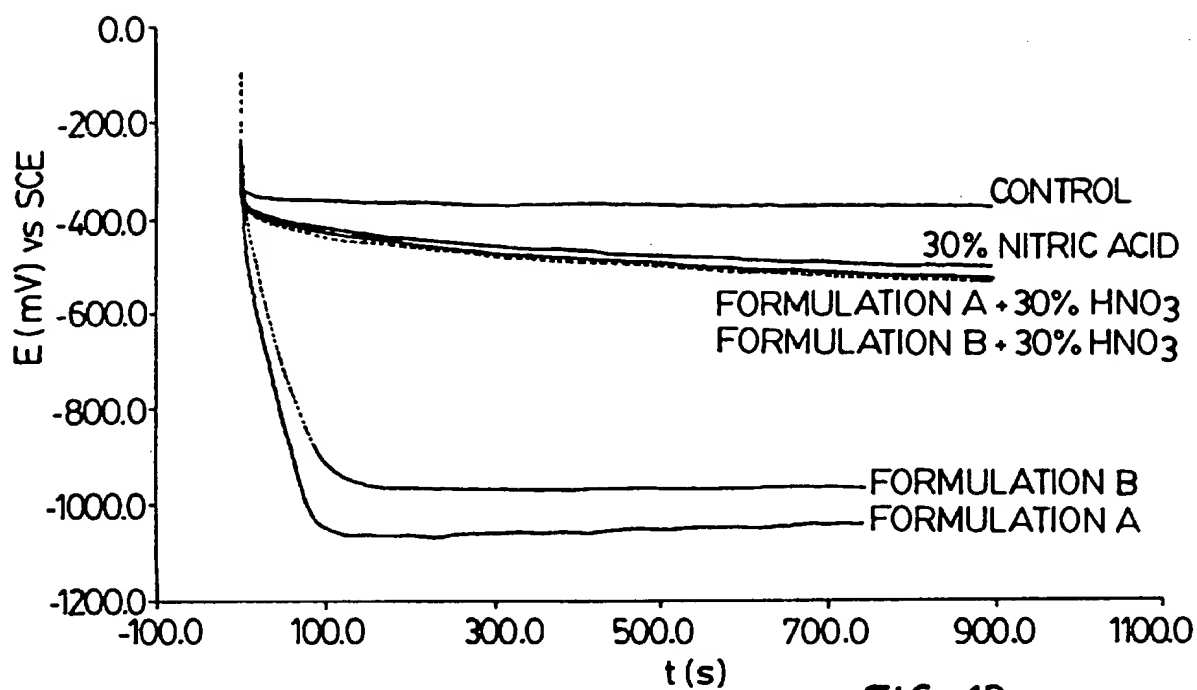


FIG. 12

WO 96/11290

PCT/CA95/00565

8/11

**FIG. 13**

WO 96/11290

PCT/CA95/00565

9/11

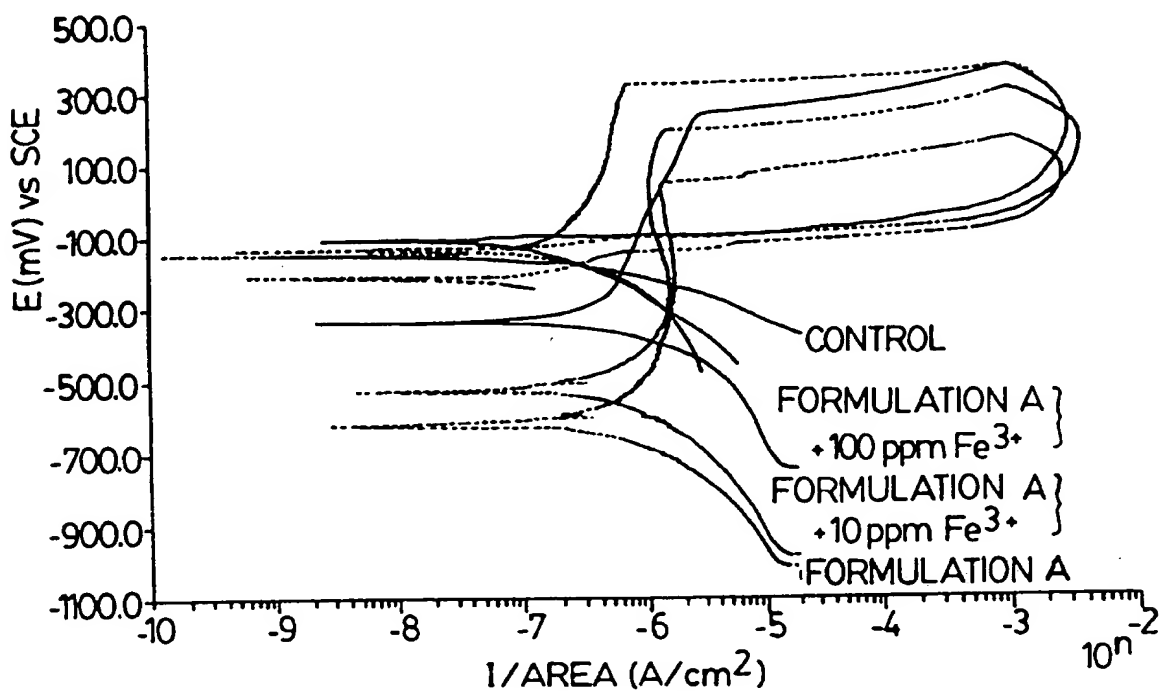


FIG. 14

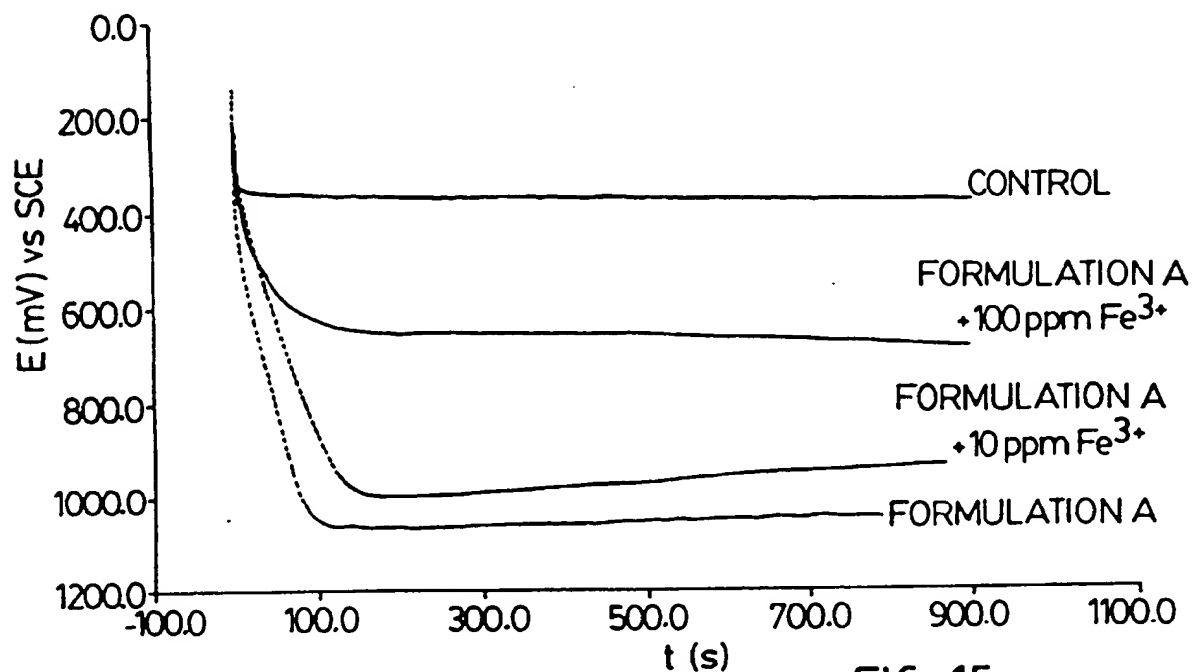


FIG. 15

WO 96/11290

PCT/CA95/00565

10/11

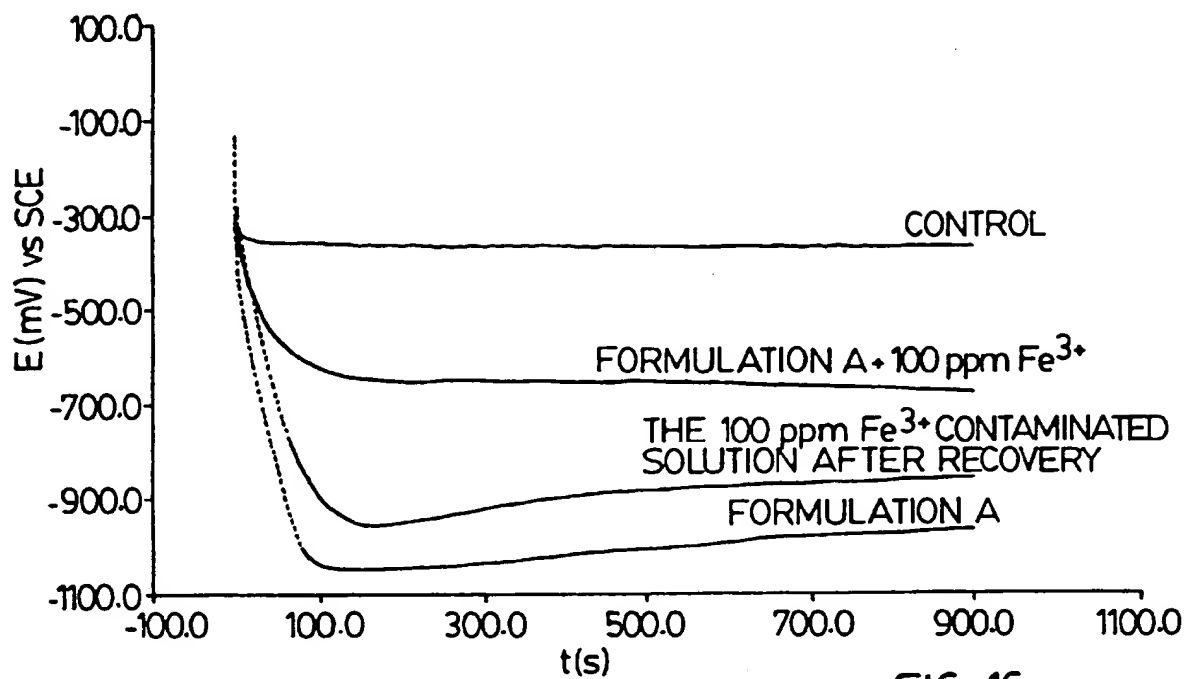


FIG. 16

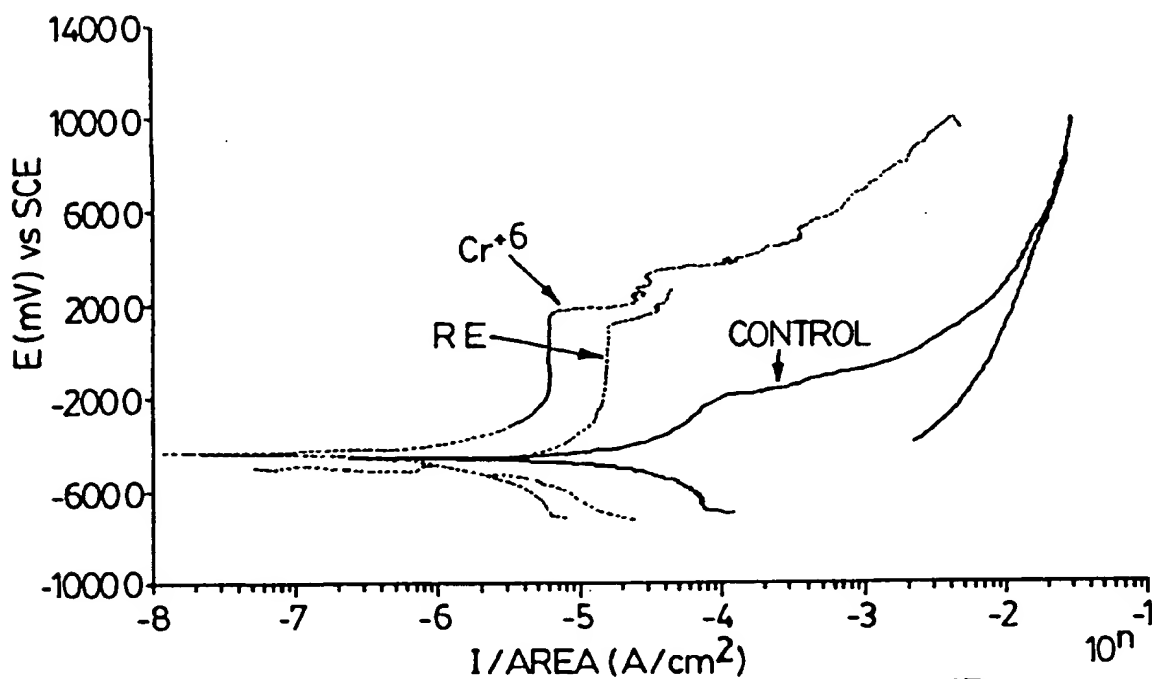


FIG. 17

WO 96/11290

PCT/CA95/00565

11/11

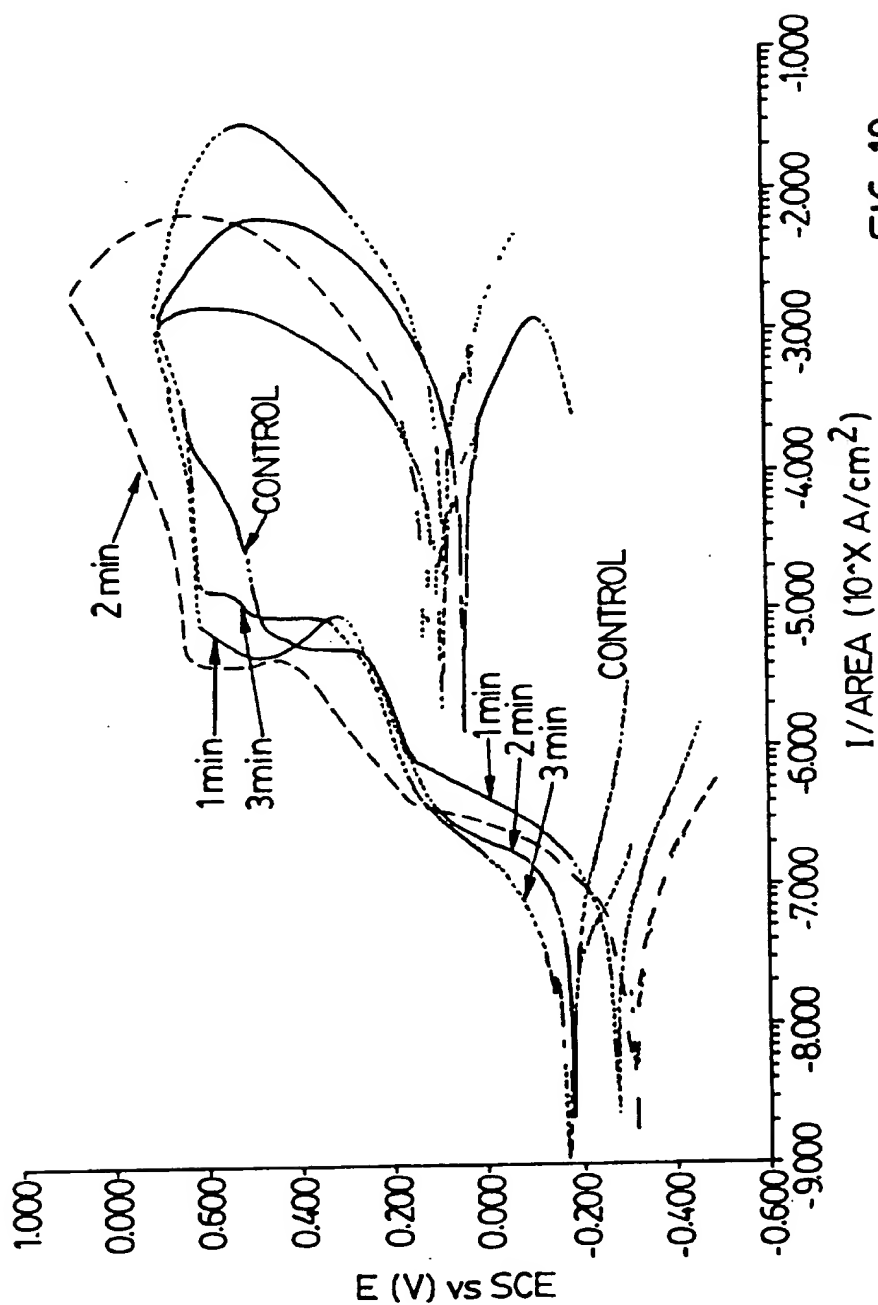


FIG. 18

INTERNATIONAL SEARCH REPORT

International Application No
PCT/CA 95/00565

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C23C22/48 C23C22/68

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,5 194 138 (MANSFELD FLORIAN B ET AL) 16 March 1993 see claims 1-8 ---	1,11
X	US,A,5 221 371 (MILLER ROBERT N) 22 June 1993 see column 4, line 35 - column 5, line 2; claim 1 ---	1,11,12, 15,16,21
P,X	WO,A,95 08008 (COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION) 23 March 1995 see page 10, line 4-18 see page 5, line 23; claims 2-5,7-15,34-38 --- -/--	1,2,6, 10,11, 13-15, 20-22,26

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

23 January 1996

Date of mailing of the international search report

05.02.96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Torfs, F

INTERNATIONAL SEARCH REPORT

International Application No
PCT/CA 95/00565

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	US,A,5 362 335 (RUNGTA RAVI) 8 November 1994 see claim 1 ---	1,11
P,X	US,A,5 356 492 (MILLER ROBERT N) 18 October 1994 see column 4, line 1-10; claim 1 ---	1,11
A	EP,A,0 331 284 (BRITISH PETROLEUM CO PLC) 6 September 1989 ---	
A	US,A,5 192 374 (KINDLER ANDREW) 9 March 1993 ---	
A	EP,A,0 367 504 (THE BRITISH PETROLEUM COMPANY) 9 May 1990 ---	
A	WO,A,88 06639 (COMMONWEALTH OF AUSTRALIA) 7 September 1988 -----	

INTERNATIONAL SEARCH REPORT

 Inter-
national Application No
PCT/CA 95/00565

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5194138	16-03-93	NONE	
US-A-5221371	22-06-93	US-A- 5399210 US-A- 5419790	21-03-95 30-05-95
WO-A-9508008	23-03-95	AU-B- 7688294	03-04-95
US-A-5362335	08-11-94	NONE	
US-A-5356492	18-10-94	NONE	
EP-A-0331284	06-09-89	ES-T- 2053968 JP-A- 1242783 US-A- 5013381	01-08-94 27-09-89 07-05-91
US-A-5192374	09-03-93	AT-T- 119949 CA-A- 2075118 DE-D- 69201707 DE-T- 69201707 EP-A- 0534120 JP-A- 5195247 KR-B- 9501218	15-04-95 28-03-93 20-04-95 07-09-95 31-03-93 03-08-93 14-02-95
EP-A-367504	09-05-90	DE-T- 68908344 WO-A- 9005204 JP-T- 4501439 US-A- 5437937	02-12-93 17-05-90 12-03-92 01-08-95
WO-A-8806639	07-09-88	AU-B- 1485888 EP-A- 0347420 JP-T- 2502655 ZA-A- 8801481	26-09-88 27-12-89 23-08-90 22-08-88